Air Improvement Resource, Inc. Comments on Air Resources Board October 2000 Draft Staff Report and October 2000 Draft Technical Support Document "The Ozone Weekend Effect in California" December 15, 2000

Air Improvement Resource, Inc. (AIR), at the request of General Motors Corporation, has reviewed the October, 2000 Draft Staff Report (SR) and Draft Technical Support Document (TSD) concerning the ozone weekend effect in California. At the outset, some comments on the ARB process of investigating the scientific evidence relating to the ozone weekend effect and developing the draft report are appropriate. AIR scientists have been following the issue for several years, attending and participating in the Work Group meetings. The ARB staff is to be commended for conducting the investigation in an open process, encouraging cooperation among scientists studying the weekend phenomenon, and sharing draft analyses for comment by the entire scientific community. AIR appreciates the opportunity to comment on the October 2000 draft material. As noted in the Executive Summary of the SR, the issue of the cause or causes of the ozone weekend effect has become an important regulatory and scientific issue.

While the draft material lays out several hypotheses that have been offered to explain the ozone weekend effect, it does not go far enough in evaluating the various hypotheses with existing data. As documented below, there is additional evidence and logical analyses that can be used to evaluate the various hypotheses. The SR concludes that there are several plausible hypotheses and not enough data to discriminate among them. The staff lays out a multi-year research program that will, hopefully, be able to test the various hypotheses more rigorously. In particular, the staff recommends a major effort to (1) develop more comprehensive day-of-the-week emission inventories and air quality data, (2) use the data to develop base cases that model current day-of-the-week behavior, and (3) design and execute modeling studies to address the alternative hypotheses. In this scheme, the evaluation of the various potential causes is put off for at least several years, perhaps more. In the meantime staff concludes:

> "Until the causes of the ozone weekend effect are determined satisfactorily, NOx reductions remain a rational and valid element of ozone control strategies in California."

Based on the analyses discussed below, AIR believes that the case for Hypothesis #1 (NOx reductions) as the primary cause of the weekend ozone increase is much stronger than the case for any of the other hypotheses. In addition, the proximate modeling currently planned by the Coordinating Research Council will be able to evaluate many of the key issues related to the various hypotheses in the near future. Thus, staff and the ARB will be able to evaluate the implications of the weekend ozone phenomenon for NOx reductions in California's ozone control strategy in the reasonably near future rather than waiting for several years.

There are several reasons why this path is preferable. First, if NOx reductions that are either currently planned or being considered are a net disbenefit for the environment, the sooner the ARB knows that the better. If the proximate modeling shows that it is a distinct possibility, the ARB should (1) set up an expedited process to complete the research plan laid out in the SR and TSD, and (2) put a hold on more NOx control until the issue is resolved. As more and more sources get controlled, the costs of emission control are rising and the number of remaining options is dwindling. If the ARB has chosen a less-than-optimum path to clean air, it will be very difficult to attain the federal and state air quality standards.

Second, because the highest ozone now occurs on weekends, the SIP updates required under California law must model weekend as well as weekday episodes. Therefore, an understanding of the implications of the weekend effect is needed as soon as possible so that SIP revisions focus on effective controls not counterproductive ones.

Third, as shown below, the weekend effect is more pronounced for 8-hour ozone concentrations than for 1-hour ozone concentrations. Therefore, if there is either a federal or California 8-hour ozone standard in the future, the likelihood of weekend episodes controlling overall emission reduction requirements will be increased.

The bulk of AIR's comments concern the SR. Unfortunately, several key pieces of information in the TSD or in the original ARB or ARB-sponsored studies are left out of the Staff Report. Thus, the draft conveys more uncertainty than is necessary based on a fuller account of the available data.

Comments on draft Staff Report

Comments on ARB strategy

The Executive Summary (ES), referring to Figure 1, indicates that the ARB strategy of concurrent reductions of the primary ozone precursors, VOCs and NOx, has "been very successful at reducing ozone concentrations in California." While ozone has been reduced substantially in California, there are several problems with the SR characterization of the "success" of concurrent VOC and NOx reductions. First, Figure 1 shows that ozone decreases occurred prior to the start of NOx controls. The TSD indicates:

> "The peak ozone concentrations in the SoCAB have declined over the years, irrespective of precursor control strategy." TSD at page 2.2-2.

In other words, ozone declined in the earlier period when VOC was being controlled and atmospheric NOx concentrations actually increased as well as in the more recent period when both VOC and NOx have been controlled. The common element is, thus, VOC control. Second, it is not clear to what extent VOC and NOx have actually been reduced in the atmosphere due to the controls applied. Unfortunately, the lack of accurate atmospheric measurements of VOCs over the years limits our ability to determine the degree of precursor control that has actually been achieved during the long-period of ozone decline. Third, without this information, it is difficult to determine whether the strategy of "concurrent" VOC and NOx control has actually resulted in "concurrent" VOC and NOx reductions or some other combination of VOC and NOx reductions. Fourth, since the chemistry of ozone formation is clearly dependent on the relative amounts of VOC and NOx, a knowledge of the balance between recent VOC and NOx reductions is critical to understanding whether California's NOx controls, once initiated, have helped or hindered the ozone reductions in various air basins.

The SR indicates that the relationship between ozone, NOx and VOCs is complex and that: "…NOx promotes ozone formation when VOCs are relatively abundant but restricts ozone formation when VOCs are relatively scarce." SR at page 1-2. This well-studied and accepted phenomenon results in the counter-intuitive result that when the ratio of VOC to NOx is low, ozone formation is VOC-limited and NOx reductions will increase ozone formation. Although the chemistry that causes this phenomenon is well-accepted, it has been difficult to deal with in the public policy arena. Many years ago, Dr. Jim Pitts wrote that this phenomenon is "the curse of control officials."

The main issue in California is whether this phenomenon is the primary cause of the weekend ozone effect or not. The SR indicates several other hypotheses that might explain the weekend ozone effect. These are discussed in detail below. In addition, the SR posits that there may be a difference between periodic NOx reductions that occur each weekend and strategic NOx reductions that would produce steady NOx reductions on both weekdays and weekends. This appears to be a distinction without a difference. As indicated by Blier and Winer,

> "Nitrogen oxides have shorter lifetimes that hydrocarbons and ozone & carryover over time periods longer than 8 hours involves mostly ozone and hydrocarbons." Blier and Winer, report to ARB, 1999 at page 1-2.

If ARB staff has specific reasons (other than the hypotheses listed) to believe that the two day reductions in NOx associated with weekend activity do not mimic longer-term NOx reduction strategies, the report should document those reasons so they may be evaluated and tested.

Magnitude of the weekend effect

The ES correctly indicates that the weekend effect is real and that ozone increases of 25 to 32 % occur in key areas in spite of the fact that NOx emissions are decreased about 25 % on Saturday and 40 % on Sunday compared to midweek levels. The magnitude of the weekend effect throughout California is displayed in the following figures developed by AIR from the California ozone data in EPA's AIRS database.

Figure 1 is a plot of 1997-1999 weekend-weekday ozone behavior versus the Design Value for 185 California sites. The weekend-weekday behavior that is plotted is the percent change in average weekend daily maximum 1-hour ozone concentrations compared to average weekday daily maximum 1-hour ozone concentrations. Note that there are a significant number of sites where the average weekend 1-hour ozone is between 10 and 30 % above the average weekday 1-hour ozone. Note also that there are no sites where the average weekend 1-hour ozone is below the average weekday by more than 10 %. Finally, note that there are a significant number of sites with demonstrably higher weekend ozone that also have design values for the federal 1-hour standard that exceed the standard.

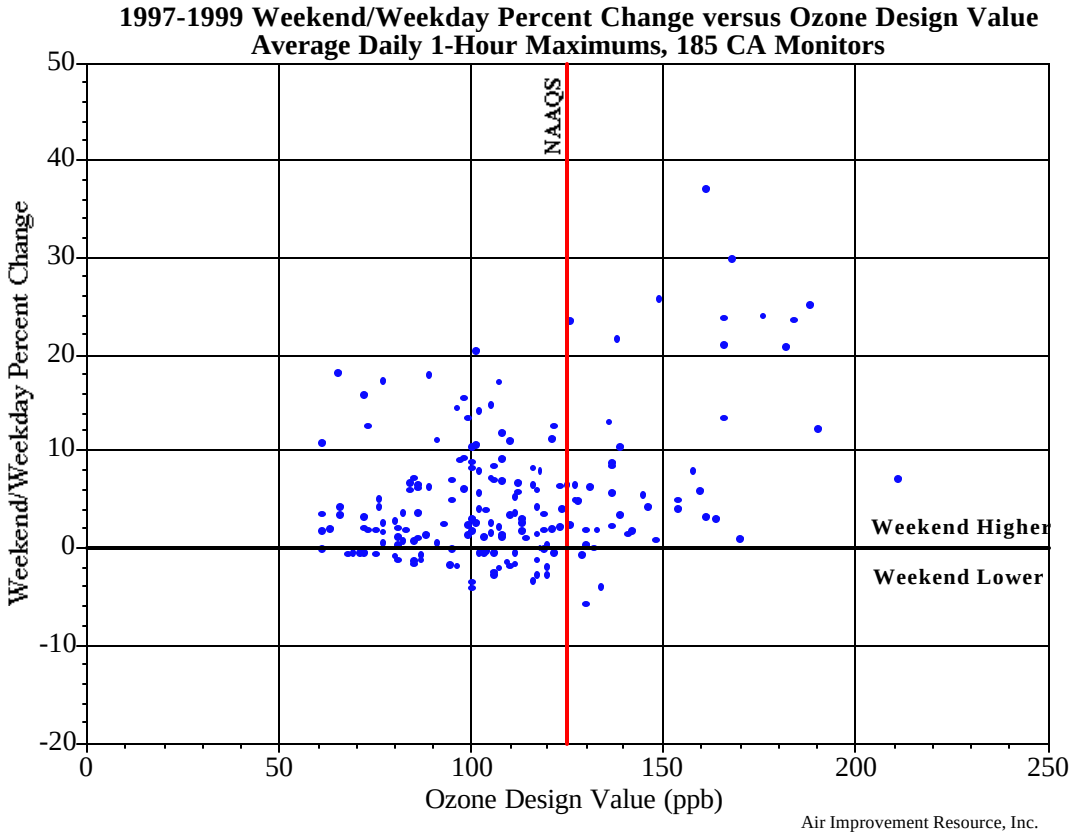

Figure 1

In Figure 2, the weekend-weekday behavior plotted is the 95th percentile of the daily 1-hour maxima. The 95th percentile was chosen to evaluate the weekend-weekday behavior for high ozone days. When compared with Figure 1, the results in Figure 2 are similar except that there is more vertical spread in the data. While there are more sites with lower 95th percentile ozone on weekends, some as much as 10 % lower, the number of sites with greater than 10 % higher 95th percentile ozone on weekends is unchanged

and the maximum impact is now between 30 and 40 % increase. Note that the sites where peak ozone is substantially greater on weekends tend to have design values above the federal NAAQS.

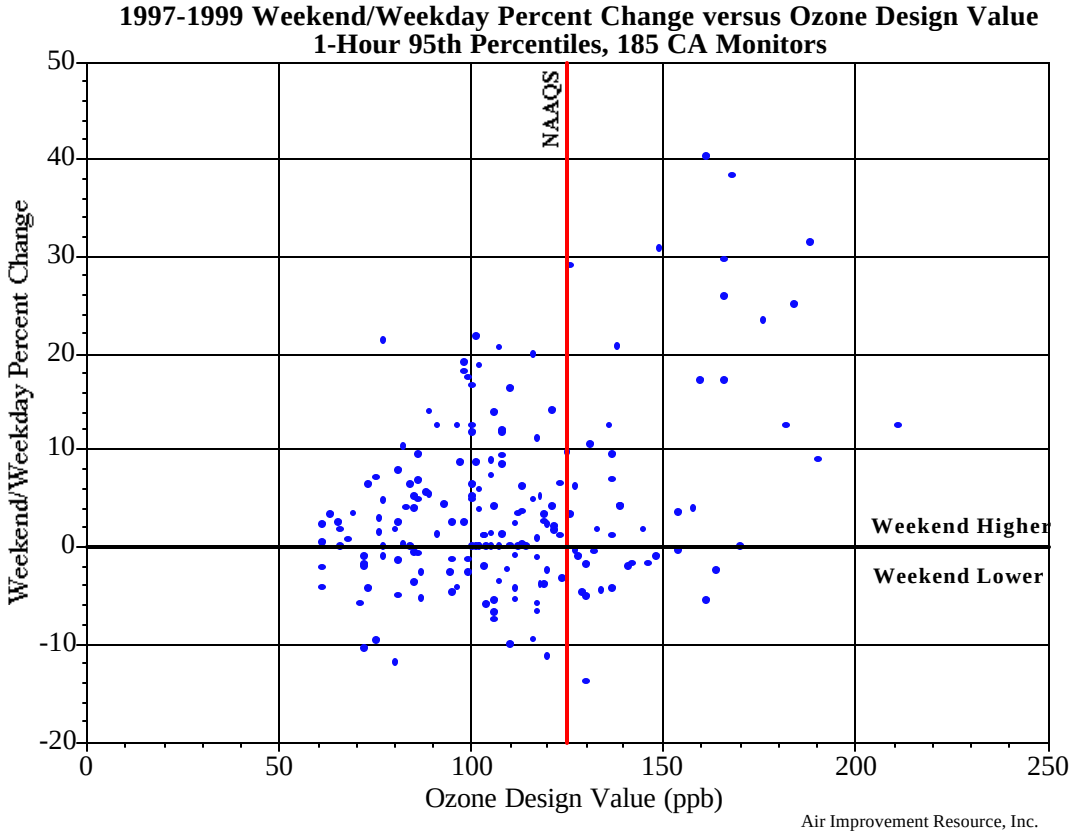

Figure 2

California has a state ozone standard of 0.09 ppm (or 90 ppb) for 1-hour. While the definition of the California ozone standard is slightly different from the definition of the federal 1-hour ozone standard, for the purposes of this display, the small difference can be ignored. Therefore, the sites to the right of a vertical line at about 90 ppb in Figures 1 and 2 are sites that exceed the California ozone standard. It is clear that higher weekend ozone is also a problem when sites that exceed the California standard are considered.

Figure 3 is a plot of weekend-weekday ozone behavior for the average daily maximum 8-hour ozone metric. Figure 4 is a companion plot for the 95th percentile 8-hour ozone concentration. The vertical lines in Figures 3 and 4 represent the now-remanded federal 8-hour ozone standard. If that standard survives the current judicial review, or if California sets an 8-hour ozone standard in the future, it is clear that higher weekend ozone will be an even greater concern for achieving any 8-hour ozone standard than it is for a 1-hour standard.

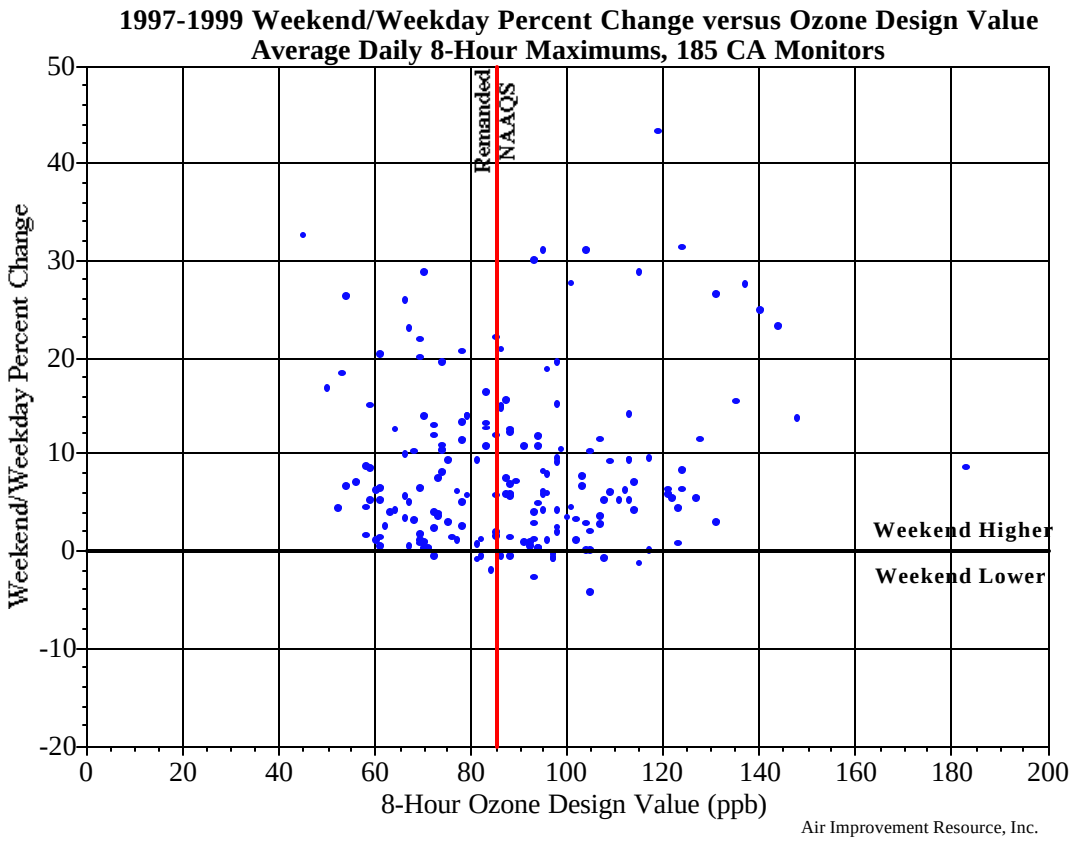
1997-1999 Weekend/Weekday Percent Change versus Ozone Design Value
Average Daily 8-Hour Maximums, 185 CA Monitors
Remanded
NAAQS
Weekend Higher
Weekend Lower
Weekend/Weekday Percent Change
8-Hour Ozone Design Value (ppb)
50
40
30
20
10
0
-10
-20
0
20
40
60
80
100
120
140
160
180
200
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Figure 3

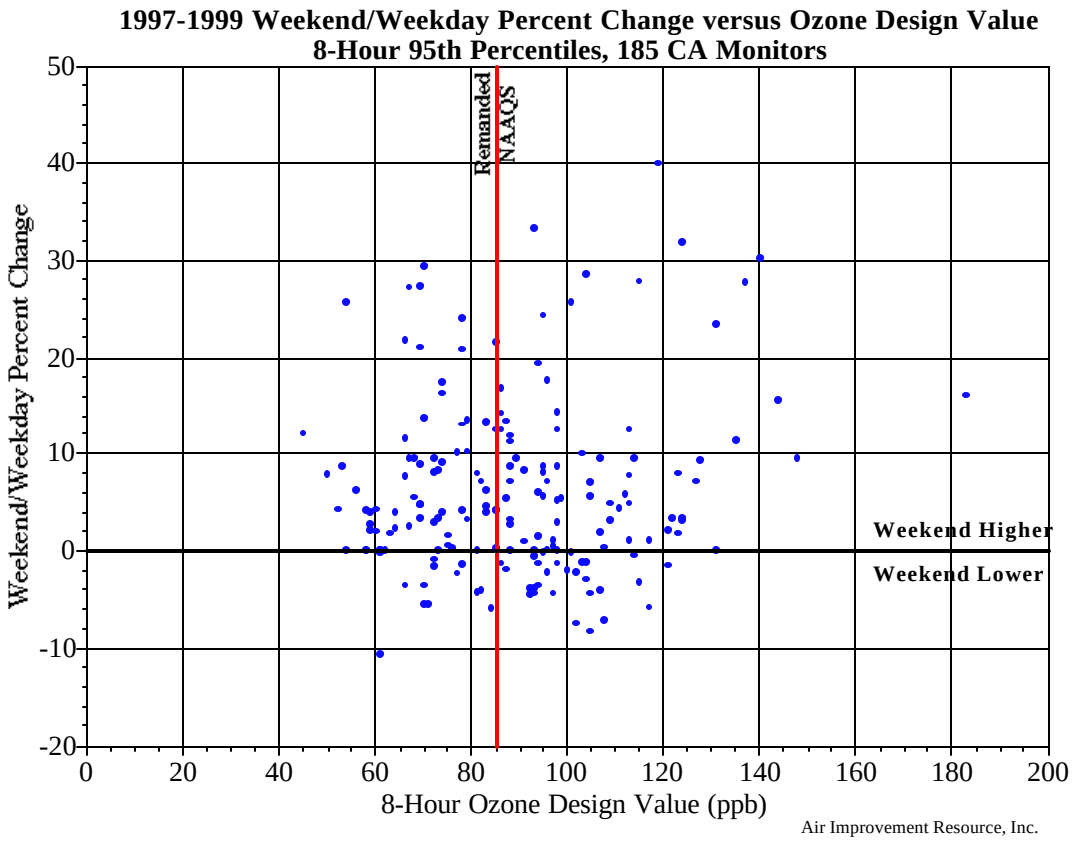

Figure 4

Several of the Findings in Chapter 3 of the SR are pertinent to our discussion of the causes of the weekend effect. In particular, Finding # 3 (that the ozone weekend effect is not static but changes with time so that ozone is now highest on Sunday throughout the Basin) is an important finding that may be useful in discriminating among potential causes. In addition, Finding # 4 (the effect tends to diminish at downwind locations) can also be an important discriminator. The combination of these findings indicates that the spatial extent of the weekend effect has grown substantially so that it now occurs at even far downwind sites as noted on page 3-3 of the SR.

Comments on causes of the weekend effect

In the section of the Executive Summary entitled "Why do some believe the ozone weekend effect implies that major reductions in NOx emissions will be counter-productive for reducing ozone," the staff summarizes three points. First, that laboratory smog chamber experiments have demonstrated the NOx benefit-disbenefit behavior that varies as a function of VOC/NOx ratio. Second, that surface VOC/NOx ratios in the SoCAB are in the range expected to show a NOx disbenefit. The text then goes on to indicate that "if this complex air basin acts like a simple smog chamber, then reducing NOx emissions should (hypothetically) promote ozone formation." Third, as discussed above, that periodic NOx reductions on weekends should mimic the steady NOx reductions from strategic regulations.

Next, the staff introduces other possible causes of the ozone weekend effect. These include the NOx-timing hypothesis, the carryover near the ground hypothesis, the carryover aloft hypothesis, the increased weekend emissions hypothesis, and the soot and sunlight hypothesis. After discussing each, the SR concludes that the increased weekend emissions hypothesis is not plausible and the carryover near the surface hypothesis is not likely to be an important factor. We agree; we will not discuss those any further.

For the remaining hypotheses that the SR indicates are plausible, we will provide additional comments. In each case, there are additional pieces of information that bear on the plausibility of the hypothesis and, therefore, need to be included in the SR and TSD.

Comments on NOx reduction hypothesis

The presentation of the scientific basis for the NOx reduction hypothesis in the body of the SR does a reasonable job of explaining the hypothesis. However, the short version in the Executive Summary that is noted above leaves the impression that the basis is only "smog chamber" experiments and specifically states that "if this complex air basin acts like a simple smog chamber, then reducing NOx emissions should (hypothetically) promote ozone formation." The synopsis of Hypothesis #1 on page 2-4, however, indicates that laboratory experiments and air quality models indicate that reducing NOx, under certain conditions, may lead to increased ozone. In fact, the basics of ozone formation that are represented in the ozone isopleths of an EKMA diagram are undergirded by more than 30 years of detailed laboratory studies of individual chemical reactions, smog chamber studies of both artificial and real atmospheric mixtures, the careful construction and testing of detailed chemical mechanisms, and numerous applications of atmospheric models that include representations of chemistry, meteorology, and transport. The air quality models that show this phenomenon include the models that are used in California's SIP development. The basic chemistry is well-understood and accepted by the scientific community as evidenced by its pre-eminent place in the discussions of ozone formation in the 1991 National Academy of Sciences Ozone Report and the more recent NARSTO Ozone Assessment. Therefore, the SR and particularly the ES should be revised to acknowledge these facts.

To fully explain the chemistry of ozone formation, the explanation of NOx-ozone chemistry on page 2-5 should be expanded to include two additional key NOx reaction paths and the concept of the photo-stationary-state. The titration reaction of NO with ozone to form NO_2 as well as the class of chain-carrying reactions of NO with radicals to form NO_2 should be included. The two reactions already noted on page 2-5 show how NO_2 can both promote and inhibit ozone formation. The two major NO reactions noted above show how NO can both promote and inhibit ozone formation. Finally, the classic concept of the photo-stationary-state should be introduced. As explained in the 1991 National Academy Ozone Report, ozone at steady-state depends on the rate of NO_2 photolysis and the ratio of NO_2 to NO. In the absence of other processes that convert NO to NO_2, the photolysis of NO_2 is balanced by the reaction of NO with ozone to re-form NO_2 and ozone does not build up. When hydrocarbons are present, however, they participate in the chain-carrying reactions that convert NO to NO_2 without using up an ozone molecule. Thus, the amount and kind of hydrocarbons present determine the ratio of NO_2 to NO which, in turn, along with the light intensity determines the ozone concentration during daylight hours. In this complex chemistry the VOC/NOx ratio plays an important role and determines whether a given change in NOx will increase or decrease ozone.

The fundamental issue is not whether the NOx-disbenefit phenomenon occurs, but to what extent it occurs in various locations in California and to what extent other hypotheses may play a role in the ozone weekend effect. As documented in the SR and TSD, the NOx reduction hypothesis is plausible and is supported by a wide range of analyses that are consistent with it being the primary cause of the weekend effect. In fact, we are not aware of any of the analyses carried out to date that are not consistent with the hypothesis. We recognize, however, that some analyses and observations are consistent with multiple hypotheses. Because of the complexities of the chemistry and meteorology involved, air quality modeling is needed to distinguish the separate effects of the various shifts in activity and emissions from weekdays to weekends.

The SR indicates that measurements of VOC/NOx ratios are an indication of VOC-limited conditions, and notes that the weekday and weekend ratios in the SoCAB are consistent with this hypothesis. But questions are raised concerning the accuracy of the ratios and whether multi-hour average ratios determined by many air parcels affect daily maximum ozone. There are, however, independent analyses with observational indicators by Blanchard that show the extent of reaction at the time of peak ozone is consistent with the hypothesis in those areas with higher weekend ozone.

As noted in Figures 1 to 4 above, the magnitude and even direction of the weekend effect varies significantly across California. The SR indicates that "concentrations of ozone precursors seem to decrease on weekends almost everywhere." (SR at page 1-3) A key issue that needs discussion in the SR is how the various hypotheses can explain these basic facts, including the changes in the weekend effect that have been observed. The atmospheric chemistry of ozone formation (the theory behind the NOx reduction hypothesis) can explain the presence of a large weekend effect in urban areas. It can explain why the effect is diminished downwind and reverses far downwind. It can also explain the growth in the spatial extent of the weekend effect. It is not clear to us how any of the other hypotheses can explain these differences.

Another key question that must be answered by this hypothesis is how ozone can be going down on both weekdays and weekends if NOx reductions can increase ozone. If the local chemical conditions are in the VOC-limited regime (above and to the left of the ridge line in Figure 2-1), equal reductions of VOC and NOx will continuously reduce ozone. However, NOx reductions, by themselves, increase ozone. The draft report of DRI/STI's retrospective analysis of ambient data used an EKMA diagram in this way to show how the chemical state of the SoCAB had changed over the years. They indicated that the VOC and NOx program had put the basin more into the VOC-limited regime (by reducing VOC somewhat more than NOx) so that the NOx-focused shift to weekends now increases ozone more broadly than before. As noted above, accurate long-term VOC data are not available. However, there are other data that corroborate this general view of what has occurred in the basin. Specialized studies that report VOC/NOx ratios and ambient trend data for individual air toxics (that are present in vehicle exhaust) indicate that VOC concentrations have been dramatically reduced over the past 35 years and VOC/NOx ratios are lower than in the past. ARB should fully evaluate these sources of data.

Comments on NOx-timing hypothesis

While there are differences in the timing as well as the magnitude of emissions between weekdays and weekends, it is unlikely that the timing differences will be able to explain the weekend effect. The ES indicates:

> "The timing difference is potentially important because laboratory experiments indicate that NOx emitted later in the day can produce ozone more efficiently."

The example discussed in the SR at page 2-7 to illustrate the effect of timing on NOx efficiency comes from Fig. 4 of Hess et al. 1992. However, the experiment (267L) that was adapted to develop Figure 2-2 had an initial VOC/NOx ratio of 51. In another experiment with an initial VOC/NOx ratio of 16.8, the rate of ozone production was <u>decreased</u> when NO was injected. ARB was aware that the experiment at a ratio of 51 is not applicable to the SoCAB. The TSD indicates:

> "When applied to the ozone weekend effect in the SoCAB, the experiments by Hess et al. have a potentially important drawback. The experiments used initial VOC/NOx ratios from 15 to 50. In the SoCAB, measured VOC/NOx ratios at the surface are generally between 5 and 10." TSD at page 6.1-14.

This is not just a potentially important drawback, it is a major flaw in the interpretation and use of the Hess et al. experiments. The discussion of the NOx-timing hypothesis should be modified to incorporate this caveat and, therefore, highly qualify the degree of plausibility of the hypothesis

In addition, the results from a series of more pertinent experiments should be added to the discussion. Kelly has carried out numerous captive air irradiations in downtown Detroit, suburban Detroit, Houston and two locations in the SoCAB.[1] These are outdoor smog chamber experiments that use natural sunlight

[1] N. A. Kelly, "Characterization of fluorocarbon-film bags as smog chambers," Environ. Sci. Technol., **16**, page 763, 1984; N. A. Kelly, "Ozone/precursor relationships in the Detroit Metropolitan Area derived from captive-air irradiations and an empirical photochemical model," J. Air Pollut. Control Assoc., **35**, page 27, 1985; N. A. Kelly, "An analysis of ozone generation in irradiated Houston air," J. Air Pollut. Control Assoc., **31**, page 565, 1981; N. A. Kelly, "Captive air irradiations in Houston, Texas," Paper No. 80-50.6,

and ambient temperatures and in which ambient air is the primary source of reactants. By operating several chambers simultaneously and by diluting the ambient mixture with clean air or by adding either VOC or NOx to different chambers, the effects of emission reductions as well as varying the VOC/NOx ratio can be determined. When Kelly conducted such experiments in rural and remote areas, the photochemistry was NOx-limited as expected. However, in the urban areas, the photochemistry was VOC-limited and NO additions reduced ozone formation. At several locations, Kelly also filled the chambers at several different times to determine the impact of timing on the ozone formation potential of the mixtures. In suburban Detroit as well as in Houston, the earliest captured mixture produced by far the most ozone. These experiments are important because they were conducted in metropolitan areas that have higher ozone on weekends throughout the area (Detroit) as well as just in portions of the area (Houston). While they do not exactly mimic the NOx-timing changes in the atmosphere, they do suggest that the photochemical potential of precursors emitted later in the day is reduced rather than increased as posited by the NOx-timing hypothesis.

Because of the complexities of ozone formation, photochemical modeling is required to fully evaluate the NOx timing hypothesis. The ENVIRON proximate modeling can be used to evaluate traffic-induced NOx changes. The activity data in the TSD suggests that there are two parts to the NOx-timing changes. First, heavy-duty truck activity and NOx emissions are expected to be substantially reduced during all hours on weekend days. Second, car and light truck activity is shifted in time because of the greatly reduced morning commute on weekend days. Since these two categories have different activity patterns and have different regulatory requirements, the modeling should evaluate the activity shifts both separately and in combination.

Comments on carryover aloft hypothesis

This hypothesis assumes that carryover aloft occurs on all days of the week, but that carryover exerts a greater influence on weekends. In both cases, the hypothesis suggests that morning concentrations of NOx titrate ozone and quench radicals. However, the higher weekday concentrations of NOx do more to reduce ozone and radicals so that they have little effect on surface concentrations. On weekends, according to this hypothesis, carryover ozone and radicals are not quenched as much and thereby cause higher surface ozone concentrations. The interactions between chemistry and meteorology that involve carryover aloft are complex. In addition, carryover in the SoCAB is more complex than in other locations because of the presence of land-sea breezes and mountains. Additional data on the composition of layers aloft would be helpful, but existing models can be applied now to determine the sensitivity of ground-level ozone to the relevant parameters.

We have three additional comments on this hypothesis-two that relate to its plausibility and one that relates to the implications of the hypothesis for regulatory NOx reductions. First, the premise for this hypothesis, that ozone carryover is the same from day-to-day but ground-level NOx emissions are different on weekdays and weekends is not correct. In reality in the SoCAB, peak ozone levels during mid-day when the atmosphere is well-mixed are now highest on Sunday. This means that the ozone available for carryover is not the same from day to day. Since ozone, on average, is lower on Mondays than on Sundays, the carryover of ozone from Sunday to Monday, on average, is substantially greater than the carryover of ozone from Monday to Tuesday. Since the morning NOx emissions on Monday and Tuesday are comparable, the impact of different levels of carryover can be compared by evaluating the levels of ground-level ozone on Monday and Tuesday afternoon. These levels are similar, which argues that carryover is not a dominant factor in determining mid-afternoon ozone levels.

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presented at the 73rd Air Pollution Control Association Annual Meeting, Montreal, Quebec, Canada, June 1980; N. A. Kelly, "Photochemical ozone formation in outdoor smog chambers and its sensitivity to changes in precursors at a suburban Detroit site," in Wolff G. T., Hanish J. L. and Schere K. L.(editors), "The Scientific and Technical Issues Facing Post-1987 Ozone Control Strategies, Air Pollution Control Association, Pittsburgh, PA, pages 110-123, 1988; N. A. Kelly and R. F. Gunst, "Response of ozone to changes in hydrocarbon and nitrogen oxide concentrations in outdoor smog chambers filled with Los Angeles air," Atmos. Environ., **24**, Part A, page 2991, 1990.

Second, if the carryover hypothesis is correct, it should be able to explain the spatial extent of the weekend effect. The hypothesis would predict that ozone should be higher on weekends at all sites with significant weekday NOx emissions and the same on weekdays and weekends at sites with little or no NOx emissions. The data, however, indicate that there are urban sites in the southeast U. S. (with high biogenic emissions) and rural sites where ozone is lower on weekends. This suggests that VOC/NOx chemistry rather than carryover is the primary cause of the weekend effect.

Finally, if the carryover aloft hypothesis is true, the NOx reduction program over the past several decades has made NOx become more efficient at making ozone on weekdays as well as on weekends. And importantly, future NOx reductions will make NOx more efficient at making ozone on both weekdays and weekends. Thus, if this hypothesis is true, the impact of carryover has been to reduce the benefits from NOx emission controls. As such, the implication of this hypothesis for regulatory NOx reductions is the same as for the NOx reduction hypothesis. In either case, less NOx means more ozone. So if further study supports this hypothesis as a significant cause or the primary cause of higher weekend ozone, the policy implications are that NOx reductions should be either avoided or approached cautiously.

Comments on soot and sunlight hypothesis

This hypothesis fits in the general category of anthropogenic changes that might affect ozone by influencing the meteorological variables that affect ozone formation. Changes in light scattering or absorption that affect solar radiation and, thereby, NO_2 photolysis or changes in temperature that influence other chemical reactions fall in this category. While the soot and sunlight hypothesis is plausible as a factor that would increase ozone on weekends, analyses carried out for ARB in an earlier study indicate that solar radiation is not significantly higher on weekends. In addition, the earlier analyses found that there is a small temperature decrease on weekends that, by itself, could reduce ozone formation on weekends by from 5 to 10 ppb. These earlier analyses are discussed in more detail below. On balance, the measured changes in meteorological variables are too small to account for the weekend effect and, if anything, may cause lower ozone formation on weekends.

In addition, because soot levels have been decreasing in California, the difference between weekday and weekend soot levels is also becoming smaller. Thus, the magnitude of any soot and sunlight effect has been getting smaller over time. This is inconsistent with the increase in the strength and spatial extent of the ozone weekend effect. Finally, since soot levels are forecast to continue decreasing, the effect will continue to get smaller in the future. For these reasons, the soot and sunlight effect should be put in the category of plausible but not likely to be a significant factor.

One of the objectives of the UCLA study (Blier and Winer, 1999) discussed on page 1-7 was:

> "To investigate, for the first time in the SoCAB, whether anthropogenic influences, for example, heat island effects and vehicle use patterns (and their resulting particulate emissions), cause differences between SoCAB micrometeorology on weekend days vs. weekdays." Blier and Winer, 1999 at page 1-2.

Blier and Winer evaluated weekday/weekend temperature differences in 5 years of data from 11 sites for the 3-month interval June 15 to September 15. They evaluated temperatures at four times of day. They concluded:

> "In 85 of the 88 cases examined, the weekday temperature was warmer than the weekend temperature. It thus appears there may have been a small difference in temperature between weekdays and weekend days that could be associated with anthropogenic influences."

The temperatures on weekdays averaged 0.6 to 0.7 degree F higher than on weekends. These small differences were not statistically significant. In addition, Blier and Winer concluded that the small magnitudes of the temperature differences suggest that any feedback on SoCAB air pollution levels will be exceedingly small. However, they did not estimate that impact. Based on earlier work by Blier and Winer and others, however, the impact would not be exceedingly small.

In their 1996 report to ARB, Blier and Winer evaluated the surface meteorological conditions on high ozone days versus average ozone days. They found that the average maximum surface temperature at all (except one) of the monitoring stations with temperature data was 9 degree F or more higher on the high ozone days. They concluded that surface heating was a significant feature associated with daily peak ozone levels. The association of high ozone with high surface temperatures has been reported by others. The U. S. EPA's July 1996 Criteria Document for Ozone summarizes a number of studies of the relationship between peak ozone and temperature. At several eastern U. S. urban sites, the rate of increase is 2 to 5 ppb per degree F. The CD also indicates that Kelly and Gunst[1] report a linear relationship between maximum ozone and temperature in outdoor captive air experiments conducted in the SoCAB. In Kelly and Gunst's experiments, the rate of increase was 10.5 ppb/degree F. This is in good agreement with the temperature effect Blier and Winer had in their comparison high and average ozone days. They report an average 11 or 12 degree F difference at various sites in the high ozone areas of the SoCAB between 28 days that averaged 150 ppb peak ozone and 28 days that had peak ozone between 250 and 330 ppb. Assuming a linear relation as found by Kelly and Gunst, the rate observed by Blier and Winer was 8 to 16 ppb/degree F. For the weekend decrease of 0.6 to 0.7 degree F reported by Blier and Winer 1999, the resulting ozone decrease would be 5 to 10 ppb. This is not an "exceedingly small" impact. And, importantly, it is opposite in direction to the ozone increases observed on weekends.

Blier and Winer (1999) also looked for a day-of-the-week signal in relative humidity and visibility data. No day-of-the-week signal was evident for relative humidity. Although there was some evidence of a day-of-the-week signal in visibility, the results were not statistically significant. In their conclusions, they indicate:

> "There was a slight tendency for lower visibility days to occur most often on Friday and Saturday at Azusa during the period 15 June to 15 September 1992-94." Blier and Winer, 1999 page 8-3

Finally, Blier and Winer evaluated day-of-the-week variation in solar radiation intensity. SCAQMD solar radiation data were available for 1994-1996 from Azusa, Pico Rivera, LA-North Main and Upland. As an initial analysis, they chose to investigate the observations from Pico Rivera. As in the temperature analysis, they evaluated the observations at four times of day. They concluded:

> "At Pico Rivera, the mean radiation intensity was found to be slightly lower on weekdays (Tuesday/Wednesday) than on weekend days (Saturday/Sunday) for each of the four hours examined, however, the result was not statistically significant…" Blier and Winer, 1999 page 8-3

The results reported in Table 5-12 of Blier and Winer indicated weekend solar radiation intensity was 1.3 % higher at 1100 PST and 1.5 % higher at 1400 PST. Because the magnitude of the effect was so small and not statistically significant, the authors did not bother to evaluate radiation intensity at the other sites where data was available. On balance, Blier and Winer found small differences in a number of meteorological variables none of which were statistically significant and some of which would tend to offset one another.

While expanded measurements and analyses can never do any harm, it is extremely unlikely that the soot and sunlight hypothesis will be able to explain any significant fraction of the weekend effect. In addition, any research program should evaluate temperature effects that would tend to offset the soot effects.

Comments on control of NOx for other purposes

The ES properly notes that secondary products of NOx emissions contribute to ambient levels of several pollutants. Of these products, NO_2 and particulate nitrate are of concern because there are air quality standards that limit their presence in the atmosphere. In the case of NO_2, both the federal and California air quality standards have now been attained in the SoCAB (as well as throughout California) so further reductions in NOx to reduce NO_2 would be counter-productive if they increase ozone. In the case of particulate nitrate, the standards are PM10 standards. Although there is not a specific standard for nitrate, nitrate is a substantial contributor to overall PM levels. Conclusion # 3 of the SR includes the statement:

> "NOx reductions are almost certainly beneficial in reducing concentrations of some other pollutants such as PM-nitrates, nitrogen dioxide and PAN." SR at page 4-2

The discussion of conclusion # 4 includes the statement:

> "Not surprisingly, nitrate concentrations tend to be lower on weekends compared to weekdays." SR at page 4-4

These statements, however, are not supported by the material in the TSD or in the Findings section of the SR. One of the bullet points in Finding # 14 is:

> "Some day-of-week comparisons of particulate matter concentrations are difficult to interpret. For example, measured PM10-nitrates in the SoCAB can be lowest on a mid-week day in some locations. No simple explanation in terms of source strengths, atmospheric chemistry, or meteorology is readily available." SR at page 3-9

More to the point is the discussion of PM in the TSD. That discussion first indicates that nitrate shows a strong spatial variation with low concentrations at coastal locations and high concentrations at inland locations. However, the TSD goes on to indicate:

> "Dichot-PM2.5, SSI-nitrate, and SSI-sulfate are virtually the "same" for all days of week." TSD at page 3.1-8

The reason for similar nitrate levels on weekends when NOx concentrations are reduced is addressed in the conclusions of Section 3.1 of the TSD. That section notes that the formation of secondary particles (such as nitrate) from precursors:

> "…is a complex non-linear process so we should not expect to see a one-to-one relationship between precursor emissions and ambient secondary PM concentrations." TSD at page 3.1-8

The text goes on to point out:

> "…there are several factors influencing the relationship between NOx emissions and particulate nitrate concentrations, which might act to reduce the impact of decreases in weekend NOx emissions on ambient 24-hour average nitrate concentrations. For example, photochemical conditions that lead to higher ozone on weekends may also increase the fraction of NOx that is converted to nitric acid and particulate nitrate." TSD at page 3.1-8

Thus, the conclusions and summary sections of the SR fail to inform the reader that (1) nitrate is not substantially lower on weekends, and that (2) the likely reason is that the higher photochemical activity on weekends (as evidenced by ozone formation) is increasing the rate of nitrate formation. The important policy implication that should be provided to the reader is that reducing NOx may not necessarily reduce nitrate concentrations if it also increases ozone formation.

Summary

The October 2000 Draft Staff Report and Technical Support Document do a good job of establishing the existence and magnitude of the ozone weekend effect. The ARB analyses also document the reduced vehicle activity and precursor concentrations that accompany increased ozone levels on weekends. The draft documents also do a good job of laying out several hypotheses for explaining the weekend effect. However, as documented above, additional information and analysis can reduce the number of plausible hypotheses so that they can be evaluated with photochemical modeling in the near future. Based the discussion in the body of these comments, several of the statements and conclusions in the Staff Report need to be revised.

For each hypothesis, several expectations are listed. It would be more appropriate to start with the findings (from ARB and other current analyses) and evaluate the hypotheses against all the findings. In this way, we believe the number of plausible hypotheses will be reduced.